r/ʌ//ᶜ
/ ʌ/ /3-. /ʌ/
)ᶜ//
` ` . / ,,./

FINAL REPORT

ON

THE DEVELOPMENT OF METHODOLOGIES AND SOLVENT SYSTEMS TO REPLACE CFC-113 IN THE VALIDATION OF LARGE-SCALE SPACECRAFT HARDWARE

NASA Research Grant Award No. NAG10-0169

October 10, 1996

Dr. Christian A. Clausen, III
Chemistry Department
University of Central Florida

Table of Contents

Abstract

The Development of Methodologies and Solvent Systems to Replace CFC-113 in the Validation of Large-Scale Spacecraft Hardware

Liquid oxygen is used as the oxidizer for the liquid fueled main engines during the launch of the space shuttle. Any hardware that comes into contact with pure oxygen either during servicing of the shuttle or in the operation of the shuttle must be validated as being free of nonvolatile residue (NVR). This is a safety requirement to prevent spontaneous combustion of carbonaceous NVR if it was to come into contact wth pure oxygen. Previous NVR validation testing of space hardware used Freon (CFC-113) as the test solvent. Because CFC-113 no longer can be used, a program was conducted to develop a NVR test procedure that uses a safe environmentally friendly solvent. The solvent that has been used in the new NVR test procedure is water. Work that has been conducted over the past three years has served to demonstrate that when small parts are subjected to ultrasound in a water bath and NVR is present a sufficient quantity is dispersed into the water to analyze for its concentration by the TOC method. The work that is described in this report extends the water wash NVR validation test to large-scale parts; that is, parts too large to be subjected to ultrasound. The method consists of concentrating the NVR in the water wash onto a bed of silica gel. The total adsorbent bed is then analyzed for TOC content by using a solid sample probe. Work that has been completed thus far has demonstrated that hydrocarbon based NVRs can be detected at levels of less than 0.1 mg per square foot of part's surface area by using a simple water wash.

THE DEVELOPMENT OF METHODOLOGIES AND SOLVENT SYSTEMS TO REPLACE CFC-113 IN THE VALIDATION OF LARGE-SCALE SPACECRAFT HARDWARE

1.0   INTRODUCTION

For the past four years, Dr. Clausen's research group at the University of Central Florida's Chemistry Department has been involved in a joint program with KSC's Materials Science Laboratory to develop a surface cleanliness validation test that does not use CFC-113. The primary direction of this work has been focused on using water as the test solvent. Equilibration of the NVR in the water was found to be facilitated by the use of ultrasonic energy. The wash solution is then tested for the presence of NVR by measuring either the total organic carbon concentration (TOC) or by measuring the intensity of ultraviolet light scattered by the wash solution (i.e., the ultrasound disperses the NVR into a colloidal state which scatters UV photons). This validation test procedure has proved to be very effective for small parts that can be placed in an ultrasonic bath.

The use of water in validating the state of surface cleanliness of large parts has not been as successful as the small part validation tests. This is primarily due to the fact that ultrasonic energy is necessary to force enough of the NVR off the surface of the part so that it can be measured in the water phase by either the TOC method or the scattering procedure. Because the large parts cannot fit into an ultrasound bath, the enhanced dispersement of the NVR does not occur; therefore, the concentration levels of NVR in the wash solution are very low. However, if the detection levels for NVR as measured by either the TOC method, or the scattering technique or some other analytical technique could be improved greatly, then the validation of large parts with a water wash may become feasible. The work that is described in this report addresses the issue of increasing the sensitivity of measuring NVR concentrations in water.

2.0   TECHNICAL DISCUSSION

Previous work has shown that when large parts that can not fit into an ultrasonic bath are subjected to a water wash, very little of any NVR present actually dissolves or is dispersed in the wash solution. Attempts to measure the NVR present in the water wash have been conducted by using a total organic analyzer (TOC). For this analysis, 100 microliters of the wash solution (i.e., typically the total volume of the wash solution is 500 mL) is injected into the TOC analyzer. Thus far, the water washes have not picked up enough NVR to be detected by this procedure. Several attempts have been made to increase the amount of NVR that the wash solution picks up. These attempts have consisted of such things as using high pressure sprays, water in combination with air, etc. Thus far, none of these attempts have been completely successful.

All carbonaceous based compounds will dissolve to a certain extent in water. For example, the solubility of alkanes in water (which are typically not thought of as a being soluble in water) can be estimated by the expression:

$$log(s) = A + B(TB) + C (TB)^2 + D(TB)^3$$

where s = solubility in water at 25°C in parts per million by weight, TB is the boiling point of the compound in K and:

A = -7.861
B = 103.032 x 10^{-3}
C = 315.247 x 10^{-6}
D = 262.558 x 10^{-9}

Thus, it can be seen that even the highest molecular weight hydrocarbons (i.e., those with high boiling points) will dissolve to a limited extent in water. The task then is to increase the sensitivity of the TOC analyzer to detect the amount that dissolves.

One approach that possesses a good potential for increasing the detection levels of NVR in a water wash is based upon concentrating the NVR on a solid absorbent, with subsequent analysis of the TOC content of the absorbent. If all of the NVR present in the 500 mL of wash water is adsorbed on the absorbent then the sensitivity of the TOC analysis will be increased by a factor of 5000. The adsorbent can be analyzed directly in the TOC unit by using a solid sample probe.

The major work of this project was directed toward developing this procedure. As might be expected when such a radically new procedure is being attempted, the developmental program went through a number of stages.

2.1   Initial Attempts at Using a Solid Adsorbent NVR Test Procedure

The first series of experiments that were conducted were concerned with establishing accuracy and precision limits for both the new students who were working on this project and also the TOC analyzer, which had been shut down for an extended period of time. Typical calibration data for standards and for NVR dispersed in water are shown in Appendix A. As can be seen from the data, carbon analyses could be performed on NVR in water with a high degree of accuracy.

The next series of experiments that were conducted were concerned with finding an adsorbent that had a low carbon content. For these experiments ten different noncarbonaceous adsorbents were collected and subjected to TOC analysis with the solid probe attachment. The samples consisted of different grades of fumed silica, various types of silica gel and several different types of molecular sieves. The carbon content of these samples ranged between 1000 ppm and 10,000 ppm, all too high to be of use in the proposed analysis methodology.

In an attempt to find a low carbon content adsorbent, several new sets of materials were collected. Some of these samples were pre-treated in a furnace at 500°C in an oxygen atmosphere prior to carbon analysis. Some of the treated samples were found to have a carbon content of less than 2 ppm. Thus, this phase of the project was successful in finding low carbon

content adsorbents that meet the needs of this methodology. In fact, later work established that with proper treatment, adsorbents with less than one ppm of carbon could be produced.

The initial experiments that were performed with the low carbon adsorbent material, was to spike the adsorbent with different types of NVR and then analyze the spiked sample for TOC by using the solid sample technique. The types of NVRs that were used ranged from hydraulic fluids to silicon oils. The experiments were run by adding known amounts of NVR to weighted amounts of silica gel. Weighed portions of the spiked silica gel were then analyzed for carbon content by using the solid sample probe of the TOC analyzer. In all of the tests that were performed, greater than 90% of the spiked NVR was accounted for.

The next series of experiments that were conducted was to use the silica gel adsorbent to recover the NVR from spiked aqueous solutions. The spiked solutions were intended to duplicate the type of samples that would be generated from a water wash of large parts that had small amounts of NVR contamination on them. The procedure consisted of adding a known amount of NVR to 500 mL of water, sonicating the solution for 15 minutes and then passing the solution through 1 gram of silica gel. The silica gel is then dried by passing N_2 through the adsorbent bed for 5 minutes. A small fraction of the silica gel is then placed into the platinum boat of the TOC solid sample analyzer. The carbon content of the sample is then measured by the TOC analyzer. The boat and sample is removed from the analyzer, cooled in a dessicator and the amount of silica gel used in the analysis is measured by weighing. The concentration of carbon in the silica gel is calculated and then used to calculate the quantity of NVR in the original 500 mL wash solution. Most of the initial work that was conducted by this procedure focused on hydrocarbon based NVRs such as hydraulic fluids (MIL-H-5606) and greases (Amoco Rykon 2). A typical calibration curve for hydraulic fluid is shown in Appendix B.

As work continued to improve upon the method of analysis, several of the procedural steps were standardized. The first procedure that was standardized concerned the treatment of the silica gel adsorbent.

The preparation of low carbon silica gel was standardized to consist of heating the silica gel to 680°C for 24 hours in a flowing stream of 99.98% pure oxygen. The carbon content of the treated silica gel typically is in the range of 1 ppm. With the furnace and combustion boats that are currently being used, 20 to 25 gram batches of the silica gel can be prepared at one time.

The procedure for concentrating the NVR from the wash solution was standardized. A disposable pipet that has previously been washed with dilute HCl is fitted with a plug of heat treated quartz wool. The pipet is then loaded with a weighed protion of treated silica gel (typically 2.0 grams). This results in an adsorbent bed that is typically 70 mm in length. The pipet is then attached to a chromatography column that has a 500 mL reservoir. The wash solution, which is 500 mL in volume, is added to the reservoir and allowed to flow through the bed at a flow rate of 2.75 mL per minute. After all of the wash solution has passed through the bed, a gentle flow of N_2 is passed through the bed to remove the remaining free water between the silica gel particles. After N_2 passage for approximately five minutes, all of the silica gel is

removed from the pipet and placed in a clean beaker, where it is mixed to produce a homogeneous sample. A fraction of the silica gel is placed in a previously weighed platinum boat. The boat and sample are then placed in the solid sample analyzer section of the TOC instrument. After analysis, the boat and sample are allowed to cool in a dessicator. After cooling, the boat and sample are weighed and the weight of the sample is calculated (typically 100 mg). A duplicate sample is then subjected to the same analysis procedure. Calculations are performed on the data so as to report the mg of carbon in the 500 mL of wash solution. If the carbon content of the NVR is known, then the mg of NVR can be calculated.

Thus far, standardization runs have been conducted with solutions of pump oil. The concentrations of the solutions have been in the range of 0.20 ppm to 5.0 ppm. Data that has been collected shows an accuracy of ± 10% with the lower detection level being in the range of 0.25 ppm.

2.2   Refinement of the solid Absorbent NVR Validation Test Procedure

In an attempt to improve on the sensitivity of the solid adsorbent method and to simplify the steps a new procedure was developed. The previous procedure consisted of analyzing approximately 200 mg of the 2.0 gram adsorbent bed. This required weighting the sample into a platinum boat. In addition, only one-tenth of the total NVR on the bed could be measured during a single analysis. The new procedure (which is described in more detail in Appendix C) consists of placing the adsorbent tube containing all of the silica gel adsorbent directly into the solid probe section of the carbon analyzer. This eliminates the need for weighing the sample and increases the sensitivity of the method by a factor of ten.

This new validation procedure is currently being tested on long sections of tubing that have been spiked with small amounts of NVR.

3.0   CONCLUSIONS

A new procedure has been developed for improving the sensitivity of the TOC method for the analysis of NVR content in wash water validation test samples. The method consists of adsorbing the NVR in the wash water onto a low carbon content adsorbent. The entire adsorbent bed is then analyzed for carbon content. The method is sensitive enough to detect the presence of a hydrocarbon based NVR at levels as low as 0.10 mg per square foot of surface area. Tests are continuing to expand the method to other types of NVR.
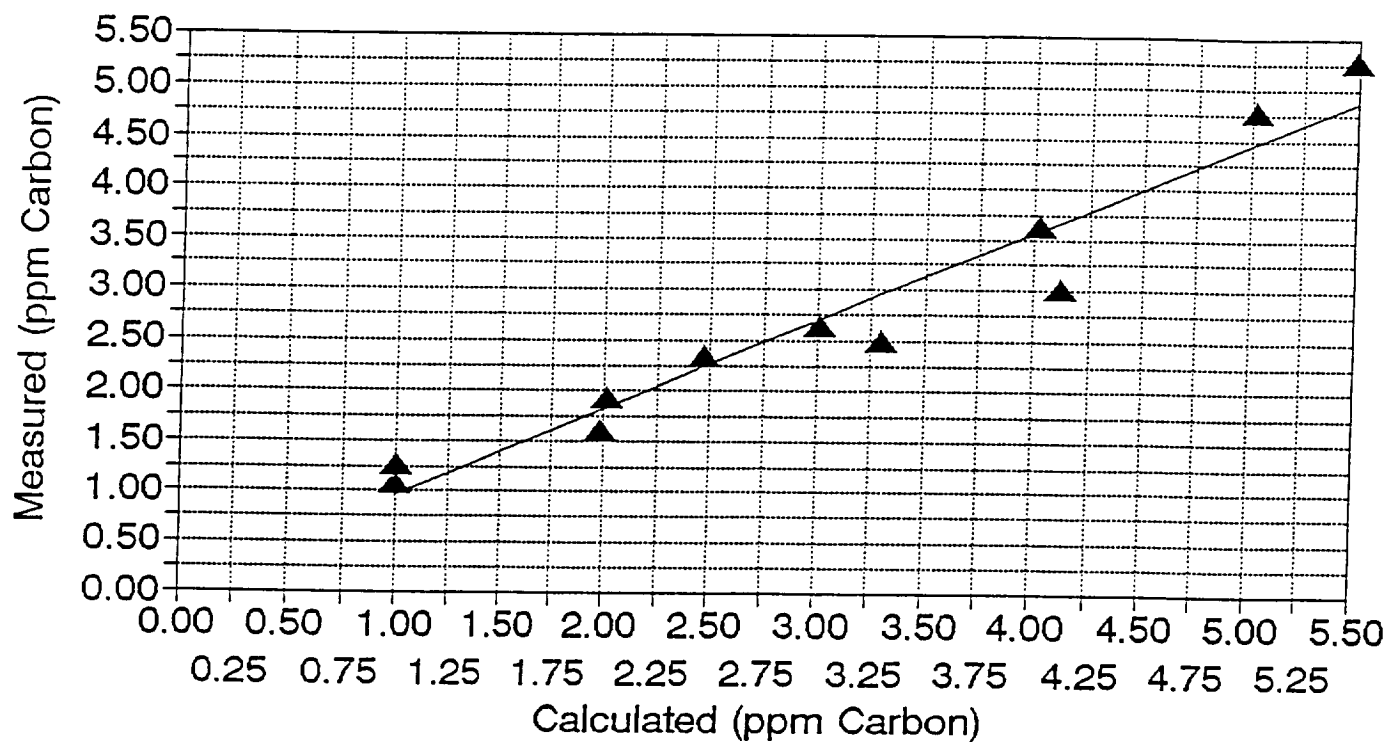
APPENDIX A

Typical Calibration Curves for NVR analysis by Using the Hitachi Model F-2000 TOC Analyzer

Graph 1

TOC Calibration for a Combination of Analysts

CALIBRATION CURVE
Carbon Analysis Combine Standards 1 & 2

Legend: ▲ Data Point —— Regression Line

Graph 1

calculated	measured	reg line
5.49	5.273	4.870342
5.02	4.778	4.460842
4.12	3.012	3.676692
4.02	3.624	3.589565
3.29	2.499	2.953532
3.01	2.641	2.709575
2.47	2.353	2.239085
2.01	1.933	1.838298
1.98	1.612	1.812159
1.00	1.255	0.958308
0.99	1.078	0.949595

Standards 1 and 2
Regression Output:

Constant	0.087031
Std Err of Y Est	0.346979
R Squared	0.941534
No. of Observations	11
Degrees of Freedom	9

X Coefficient(s)	0.871277
Std Err of Coef.	0.072371

Graph 2

TOC CALIBRATION CURVE
Carbon Analysis **NVR** Standards

Measured (ppm Carbon) one injection

5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00

0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50
0.25 0.75 1.25 1.75 2.25 2.75 3.25 3.75 4.25 4.75 5.25

Calculated (ppm Carbon)
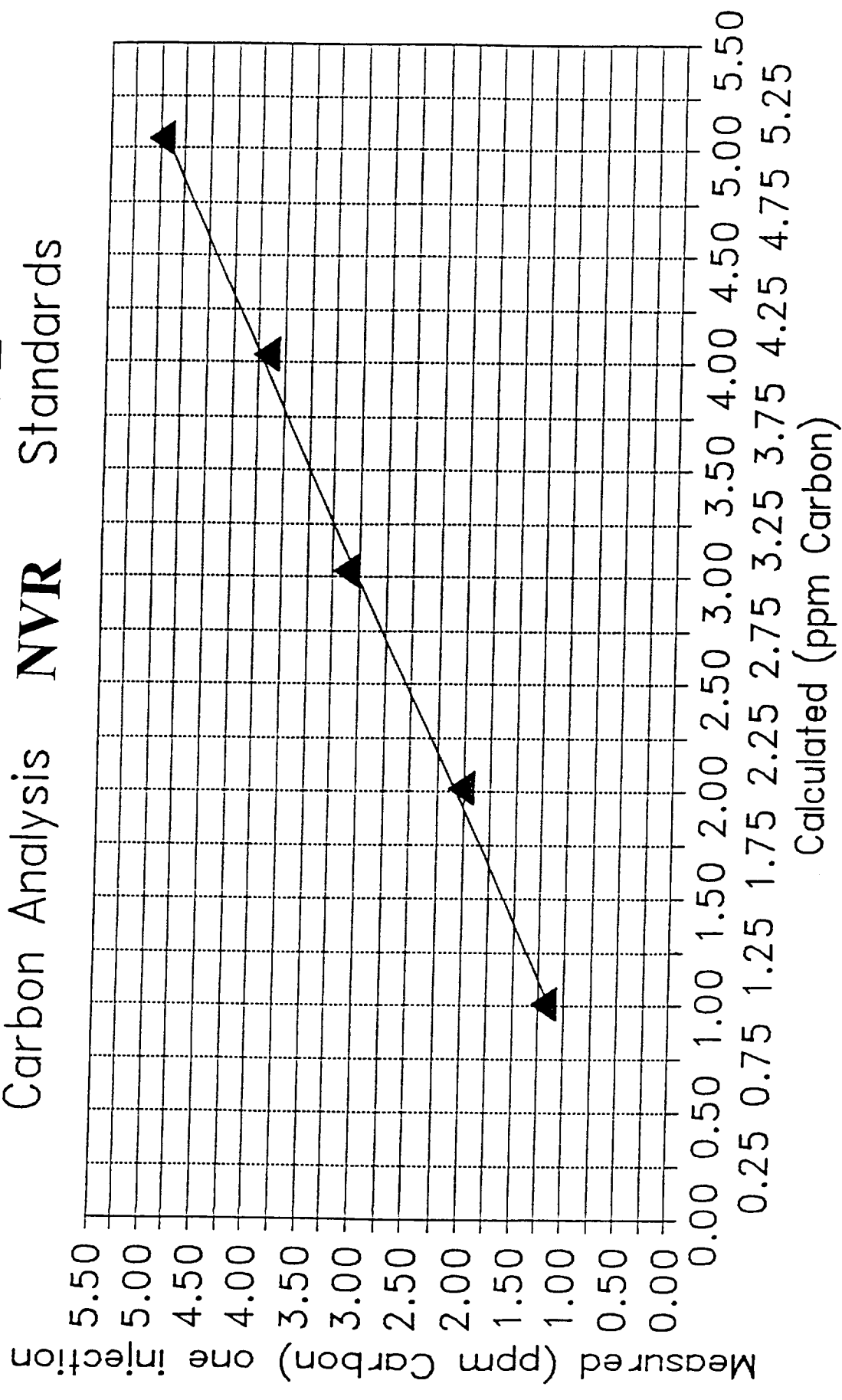
▲ Data Point   — Regression Line

Graph 2

calculated	measured	reg line
1.01	1.194	1.1518
2.02	2.02	2.0997
3.03	3.116	3.0476
4.04	3.929	3.995501
5.05	4.979	4.943401
1009	1017	

Regression Output:

Constant	0.2039
Std Err of Y Est	0.07853
R Squared	0.997945
No. of Observations	5
Degrees of Freedom	3

X Coefficient(s)	0.938515
Std Err of Coef.	0.024588

APPENDIX B

A Typical Calibration Curve for an NVR Adsorbed on a Silica Gel Bed from an Aqueous Wash Solution

ppm C Std	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Avg TC (ppm)
4.98	5.641	5.482	5.466			5.53 +/- 0.097
3.984	4.844	4.861	4.67	4.804		4.795 +/- 0.087
2.988	3.659	3.648		3.6		3.635 +/- 0.031
1.992	2.568	2.61	2.565			2.581 +/- 0.025
0.996	1.547	1.598	1.616			1.587 +/- 0.036
0.747	1.34	1.352	1.256	1.262		1.303 +/-0.05
0.498	1.106		1.068	1.089		1.088 +/- 0.019
0.249	0.784	0.743	0.702	0.776		0.751 +/- 0.037
0.0996	0.581	0.721	0.657	0.551	0.671	0.636 +/- 0.069
DI Water-pH	0.504	0.492	0.512			0.503 +/- 0.01

				C Std (ppm)	Avg TC (ppm)	Avg TC - DI water
				4.98	5.53	5.027
				3.984	4.795	4.292
				2.988	3.635	3.132
				1.992	2.581	2.078
				0.996	1.587	1.084
				0.747	1.303	0.8
				0.498	1.088	0.585
				0.249	0.751	0.248
				0.0996	0.636	0.133
				DI Water-pH	0.503	

Calibration Curve for the Determination of ppm C

$y = 1.0273x + 0.0439$
$R^2 = 0.9982$

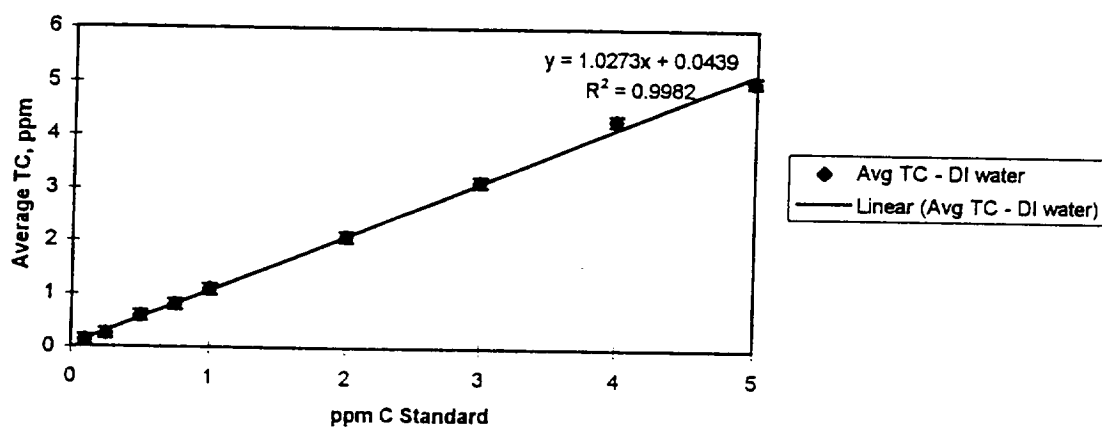- Avg TC - DI water
— Linear (Avg TC - DI water)

Figure 1. Typical calibration curve for Hydraulic Fluid
using a solid adsorbent concentrating proceedure

APPENDIX C

A Test Procedure for Measuring the NVR Content in a Water Wash Sample by the Analysis of Carbon Adsorbed on a Silica Gel Bed

Test Procedure for Analyzing NVR on a Silica Gel Adsorbent

Procedure

A quartz sample tube was designed which included a slit in which the platinum wire of the boat injector could be attached. The prepared sample tubes dimensions are: 7 mm inside diameter, by 9 mm outside diameter, by 50 mm in length. The quartz tube was weighed with two tuffs of quartz wool. The tube was filled with 914 mg (dry weight) of silica gel and held in the tube by the two tufts of quartz wool. A 500 mL separation funnel was set up with a sample tube holder. The sample tube holder was made by attaching a Teflon burette to each end of an approximate 70 mm length of burette tube with seals at each end made of cut pieces of Tygon tubing. The seals were to prevent blow-by of the sample around the silica through the 5 mm slit in the quartz sample tube. A nitrogen gas supply, utilizing a gas flow meter, was attached to the top of the separation funnel to prevent CO_2 contamination of the sample tube silica, to maintain a constant flow rate, and to aid in drying the sample silica gel. All nitrogen supply lines were cleaned and attached to the analyzer with a 200 mL per minute flow rate to determine if any residual carbon remained in the lines.

The Dohrmann DC-190 analyzer was calibrated, in the syringe mode, and tested for accuracy between 4 and 1 ppm. After analyzing a pump oil dilution and determining its concentration as approximately 65 ppm total carbon (TC), six 500 mL samples were prepared from aliquots as follows: sample #1, 1.3 ppm; sample #2, 0.65 ppm; sample #3, 0.13 ppm; sample #4, 0.13 ppm; sample #5 0.078 ppm; and sample #6 0.026 ppm total carbon. The samples were analyzed to document the concentrations.

The quartz sample tube was baked to a baseline value of approximately 0.23 µg/g. After baking, the tube was cooled to room temperature and inserted into the sample tube holder. The sample tube holder was attached to the separatory funnel and 500 mL of the pH 3 de-ionized water, used to make the dilutions, was passed through the sample tube and analyzed, in the boat mode, to determine a blank. Each sample was then independently ran through the sample tube and analyzed for total carbon.

Equipment

A quartz sample tube [Figure 1] was designed which included a slit in which the platinum wire of the boat injector could be attached. The prepared sample tubes dimensions are: 7 mm inside diameter, by 9 mm outside diameter, by 50 mm in length. The quartz tube was weighed with two tuffs of quartz wool. The tube was filled with 914 mg of silica gel and held in place by the two tufts of quartz wool.
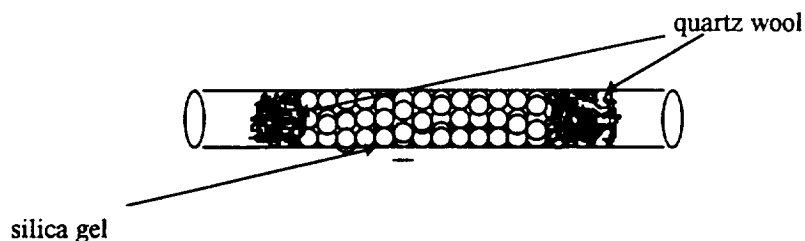

Figure 1: Quartz sample tube.

A sample tube holder [Figure 2] was made by attaching a Teflon burette fitting to each end of an approximate 70 mm length of burette tube with seals at each end made of cut pieces of Tygon tubing. The seals were to prevent blow-by of the sample around the silica through the 5 mm slit in the quartz sample tube.
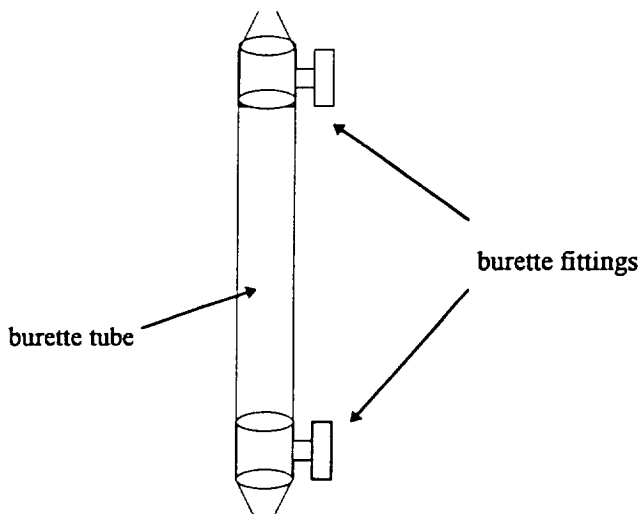

Figure 2: Sample tube holder.

2

The sample apparatus [Figure 3] included the sample tube, sample tube holder, and a separatory funnel setup. A nitrogen gas supply, utilizing a gas flow meter, was attached to the top of a separation funnel to prevent CO_2 contamination of the sample tube silica, to maintain a constant flow rate, and to aid in drying the sample silica gel. All nitrogen supply lines were cleaned and analyzed for residual carbon.
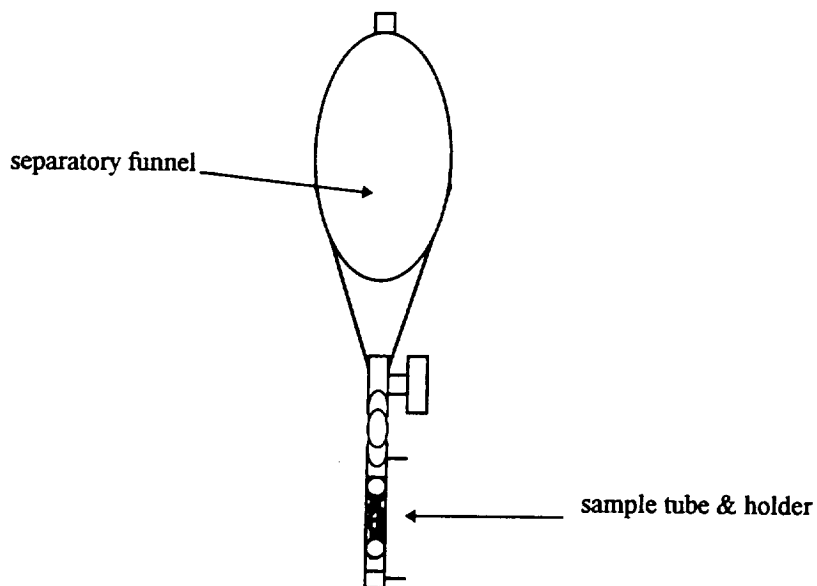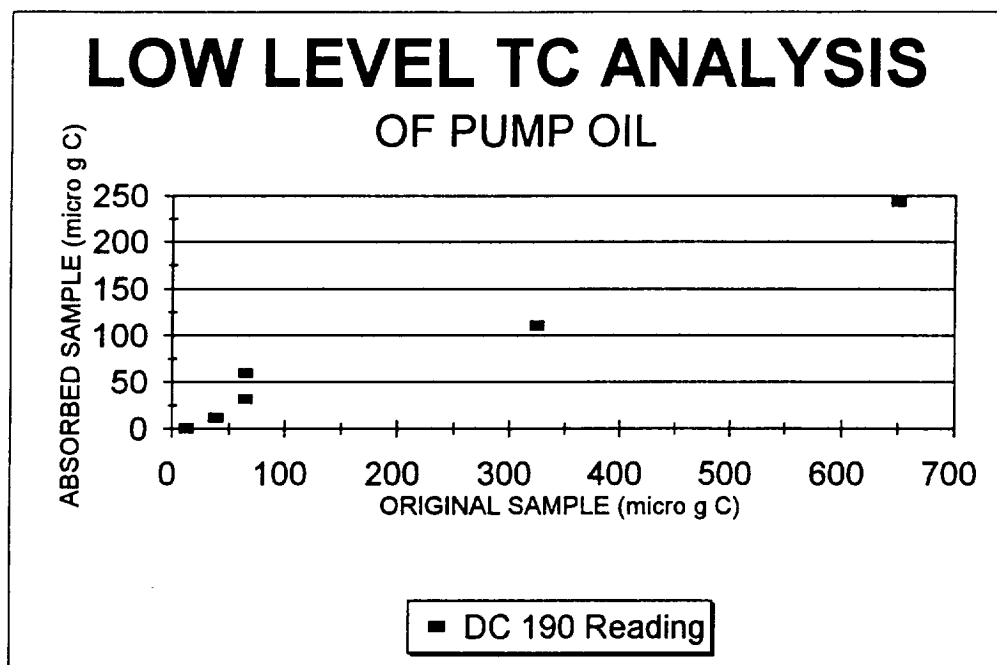

Figure 3: Sample apparatus.

Results:

The nitrogen gas supply tested to 0.6 µg/g. The sample analysis is depicted in the following table and graph:

LOW LEVEL TC ANALYSIS
OF PUMP OIL

■ DC 190 Reading

Graph 1: Shows a proportional decrease in the absorbed sample versus the original sample. The point which corresponds to 65 µg C, as absorbed sample, may have been contaminated when a fly landed on the sample tube prior to analysis.

SAMPLE ANALYSIS					
sample #	sample (ppm C), α	sample (µg C), α	silica absorbent (g)	absorbed (µg/g C), β	absorbed (µg C), γ
1	1.3	650	0.914	265.8	242.9
2	0.65	325	0.914	120.8	110.4
3	0.13	65	0.917	65.00	59.60
4	0.078	65	0.917	34.60	31.72
5	0.078	39	0.922	12.53	11.55
6	0.026	13	0.922	0.028	0.026

α – carbon content of original sample
β – carbon content absorbed per gram of silica (calculated from TC analyzer reading)
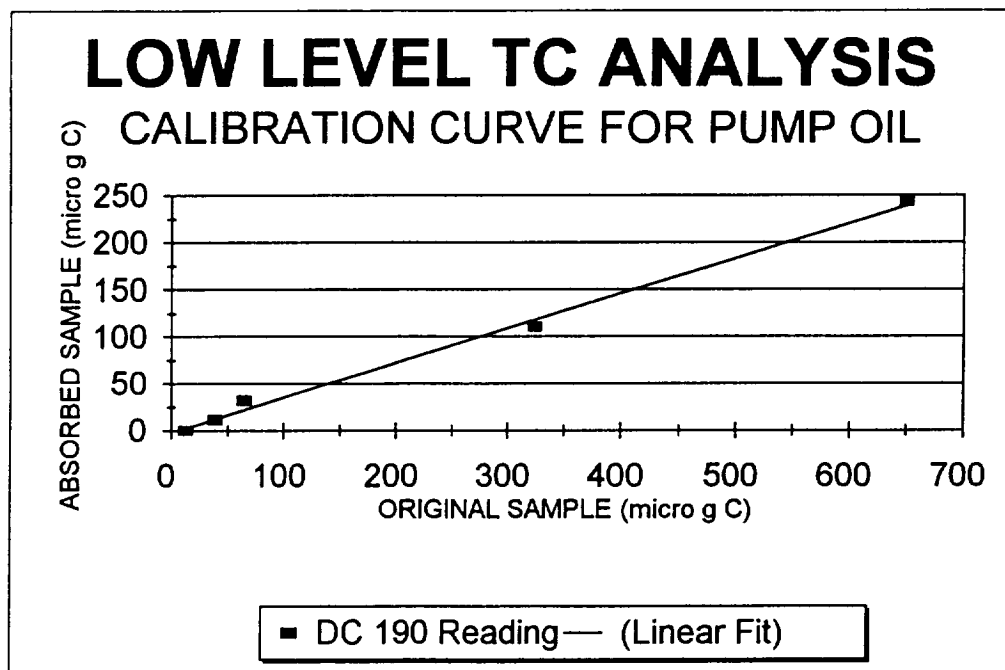γ – carbon absorbed

Table 1

Analysis:

An analysis of the data in [Table 1] and [Graph 1] shows that a decrease in the absorbed concentration is proportional to that of the original samples when sample #3 is omitted. The water blank was calculated by subtracting the lowest observed water analysis from the sample analysis and adding the average analysis taken when moving the sample tube in and out of the analyzer.

The lowest reading achieved thus far is equivalent to reading a sample with a total carbon content of 13 µg C. This corresponds to a calculated absorption of 0.026 µg C.

Conclusion:

This technique seems to be a very accurate means of determining low level carbon concentrations in water. The 0.028 μg C reading would appear to be near the threshold or end point for the analysis technique since the water blanks analyzed varied by +/- 3 μg C. Sample #3 is omitted in preparation of a calibration curve for pump oil analysis. For pump oil analysis [Graph 2] and [Table 2] will be used.

Graph 2: Calibration curve for determining carbon in pump oil dilutions.

SAMPLE ANALYSIS					
sample #	sample (ppm C), α	sample (μg C), α	silica absorbent (g)	absorbed (μg C), β	absorbed (μg C), γ
1	1.3	650	0.914	265.8	242.9
2	0.65	325	0.914	120.8	110.4
4	0.13	65	0.917	34.60	31.72
5	0.078	39	0.922	12.53	11.55
6	0.026	13	0.922	0.028	0.026

α – carbon content of original sample
β – carbon content absorbed per gram of silica (calculated from TC analyzer reading)
γ – carbon absorbed by silica

Table 2